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(71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors: RAMANAN, Genapathy, Venkata; 1803, Pomelo Street, Dasmarinas Village, Makati, Metro Manila 1222 (PH). ROBLES, Eric, San, Jose; Valero Plaza Unit 504, 124 Valero Street, Makati City, 1200 (US). TEE, Johannson, Jimmy; 19, Wilson Street, Greenhills, San Juan, Metro Manila 1222 (PH). HIDALGO, Noe, Ongcoy; 34 Countryside Subdivision, Barangka Ibaba, Mandaluyong City, 1550 (PH). DU VAL, Dean, Larry; 5–16–1801, Koyo–cho Naka, Higashinada–ku, Kobe 658 (JP). PEREZ, Barbara, Cajanding; 233 C M. Concepcion Street, San Joaquin, Pasig City, 1601 (PH). CASTRO, Jerome, Macaisa; BLK 25 Lot 17, J. Fuentes Street, Chrysanthemum Village, San Pedro, Laguna, 4023 (PH). MONROY, Teddy, Go; 727 Interior 1, T. Alonzo Street, Santa Cruz, Metro Manila, 1222 (PH).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).

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(57) Abstract

The present invention relates to a process for making a synthetic laundry detergent bar composition having improved physical properties wherein a calcium salt and siliceous material complex is formed in situ. The present invention also relates to bar compositions made by the process described above.

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LAUNDRY DETERGENT BARS WITH IMPROVED PHYSICAL PROPERTIES

FIELD OF THE INVENTION

This invention relates to a method of making a laundry detergent bar composition comprising synthetic anionic detergent surfactant having improved physical properties.

BACKGROUND OF THE INVENTION

In societies where mechanical washing machines are not common, laundry detergent bars comprising synthetic organic surfactants and detergency builders are used in the laundering of clothes. Technical developments in the field of laundry detergent bars have concerned formulating bars which are effective in cleaning clothes; which have acceptable sudsing characteristics in warm and cool water and in hard and soft water; which have acceptable in-use wear rates, hardness, durability, and feel; which have low smear; and which have a pleasing odor and appearance. Methods for making laundry detergent bars are also well known in the art. Prior art disclosing laundry bars and methods for making laundry bars include: U.S. Pat. 3,178,370, Okenfuss, issued April 13, 1965; and Philippine Pat. 13,778, Anderson, issued September 23, 1980.

Laundry bar compositions are commonly used in countries having high humidity, such as in the Philippines, India, and Latin America. Consumers often launder clothes outside and therefore often store the laundry bars outside. Such bars which are stored at high humidity conditions tend to become soft and mushy when exposed from the wrapper. Although not intended to be limited by theory, the bars tend to absorb

moisture in such high humidity conditions. It is undesirable for consumers to handle such mushy bars. Furthermore, consumers find it difficult to wash clothes properly using soft bars since the bar must be sufficiently hard to rub directly against the clothes.

In addition, since bars are used for more than one wash load, after one use, the bar is stored (usually outside) and reused. The used bars which became wet during the wash do not dry adequately after use, especially in high humidity conditions. Not only does it stay wet and mushy after use, but the bars may continue to absorb additional moisture from the high humidity conditions of storage after use.

It has now been found that the in-situ formation of a complex between calcium salt and siliceous material during bar processing improves the physical properties of synthetic laundry bar compositions. One benefit is that the bars have significantly less moisture absorption, especially at high humidity conditions, which leads to a good rate of drying of the surface of the bar. In addition, such bar compositions of the present invention have improved hardness of the bar, thereby retaining the structural integrity during use and transportation. Furthermore, such compositions have reduced bar solubility, wherein it is harder for the bar to dissolve after becoming wet during the washing process.

SUMMARY OF THE INVENTION

The present invention relates to a process for making a synthetic laundry detergent bar composition comprising the steps of:

a. forming a mixture comprising a neutralized anionic synthetic detergent surfactant selected from the group consisting of alkyl sulfate, linear alkyl benzene sulfonate, and mixtures thereof, a phosphate detergency builder, calcium salt, siliceous material, and optionally other ingredients;

wherein the calcium salt and siliceous material form a complex in-situ; and

wherein the phosphate detergency builder is added after the addition of calcium salt and siliceous material; and

b. forming into bars;

wherein the bar composition comprises at least 6% of the anionic synthetic detergent surfactant in the final bar composition.

The present invention also relates to bar compositions made by the process described above.

DETAILED DESCRIPTION OF THE INVENTION

While this specification concludes with claims distinctly pointing out and particularly claiming that which is regarded as the invention, it is believed that the invention can be better understood through a careful reading of the following detailed description of the invention. In this specification, all percentages, ratios, and proportions are by weight, all temperatures are expressed in degrees Celsius, molecular weights are in weight average, and the decimal is represented by the point (.), unless otherwise indicated.

All documents referenced herein are incorporated by reference.

Anionic synthetic detergent surfactants

The composition of the present invention comprises at least 6% anionic synthetic detergent surfactant, by weight of the total bar composition, selected from the group consisting of alkyl sulfate, linear alkyl benzene sulfonate, and mixtures thereof. Preferably the bar composition comprises at least 10%, more preferably from about 15% to about 30% anionic synthetic detergent surfactant, by weight of the total bar composition.

Anionic synthetic detergent surfactants which are suitable for use herein include the water-soluble salts, preferably the alkali metal, ammonium and alkylolammonium salts of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_{8-18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220.099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 10 to 18, abbreviated as C_{10-18} LAS. The alkali metal salts, particularly the sodium salts of these surfactants are preferred. Alkylbenzene sulfonates and

processes for making them are disclosed in U.S. Patent Nos. 2,220,099 and 2,477,383.

Mixtures of the above types of anionic surfactants are preferred. Specifically, preferred anionic surfactants are C_{10-18} linear alkyl benzene sulfonates, C_{10-18} alkyl sulfates, and mixtures thereof. One preferred composition comprises from about 10% to about 30% LAS, by weight of the total bar composition for a primarily LAS-surfactant based bar. Another preferred composition comprises a mixture of LAS:Alkyl sulfate in a ratio of from about 10:90 to about 50:50, preferably from about 20:80 to about 40:60. The anionic surfactant can be introduced into the process in its neutralized salt form or it can be introduced in its acid form and neutralized in situ prior to the addition of the calcium salt, siliceous material, and phosphate builder.

Phosphate Detergency Builder

The laundry bars of the invention contain at least 3%, preferably from about 5% to about 50%, more preferably from about 10% to about 30% phosphate detergent builder, by weight of the total bar composition. These detergent builders can be, for example, water-soluble alkali-metal salts of phosphate, pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof. Preferred builders are a water-soluble alkali-metal salt of tripolyphosphate, and a mixture of tripolyphosphate and pyrophosphate. Specific preferred examples of builders include sodium tripolyphosphates (STPP) and tetra sodium pyrophosphates (TSPP), and mixtures thereof.

Formation of a complex in-situ

An effective amount of a complex formed in-situ via the reaction of a calcium salt and a siliceous material improves the bar physical properties. Preferably the amount of calcium salt added, by weight of the total bar composition is from about 0.5% to about 10%, more preferably from about 1% to about 5%. Preferred calcium salts are CaO, $Ca(OH)_2$, $CaCl_2$ and $CaSO_4$, and mixtures thereof. The calcium salt preferably is in a fine powder form, preferably with a particle size of from about 60 mesh to about 300 mesh and more preferably from about 100 mesh to about 200 mesh.

Siliceous materials

Siliceous materials include silica in finely divided form, such as micronised silica gels, precipitated silicas and silica aerosols. It also includes silicates, which may be water-soluble metal, alkaline or neutral

silicates. Other siliceous materials include polymeric silicates and amorphous synthetic sodium aluminosilicates, serpentine-kaolin, talc-pyrophyllite and smectite clays. Clays include kaolin, talc, saponites, and montmorillonite.

Preferably the amount of siliceous material added, by weight of the total bar composition, is from about 0.5% to about 25%, more preferably from about 1.0% to about 15% and most preferably from about 1.5% to about 10%. Preferably, the siliceous material is sodium silicate, with a SiO_2/Na_2O molar ratio of from about 2:1 to about 3:1. The most preferred material is alkaline sodium silicate with a SiO_2/Na_2O molar ratio of about 2:1.

Adjunct Ingredients

The detergent bars of the present invention can optionally contain a polyol and a cross-linking agent added to the mixture, preferably the polyol and a cross-linking agent added to the mixture prior to the addition of the calcium salt and the silaceous material; more preferably, the polyol and the cross-linking agent are added after the neutralization of the anionic synthetic surfactant and prior to the addition of the calcium salt and the silaceous material.

In addition to adding the polyol and the cross-linking agent at this step, they can alternatively be added at any other step. Furthermore, the polyol and cross-linking agent can also be included for multiple purposes, for example, polyethylene glycols can also be included herein, as described below, as soil suspension agents. The polyol can be included at this step at levels up to about 10%, preferably from about 0.1% to about 5%, by weight of the total bar composition. Similarly, the cross-linking agent can be included at this step at levels up to about 10%, preferably from about 0.1% to about 5%, by weight of the total bar composition. Polyols useful herein include substituted polyols, unsubstituted polyols and mixtures thereof; preferably sorbitols, polymers with free hydroxyl groups, substituted polyols, and mixtures thereof; more preferably polyethylene glycols, polyvinyl alcohol, and mixtures thereof.

Cross-linking agent preferred for use herein include an oxophile, an acid, and mixtures thereof. Oxophiles are defined herein as compounds having an affinity to either hydrogen bond or covalently bond with oxygen atoms. Oxophiles useful in the present invention include aluminates, silicates, borates, and mixtures thereof; preferably planar oxophiles,

tetrahedral oxophiles, and mixtures thereof; more preferably sodium silicate, zeolites, disodium borate (Na_2BO_4), silicon dioxide (SiO_2), and mixtures thereof. Oxophiles can be added in either the solid or liquid form, or dispersed or dissolved in water. Acids useful herein include organic acids, inorganic acids, and mixtures thereof; preferably planar acids, tetrahedral acids, and mixtures thereof; more preferably boric acid, maleic acid, phosphonic acid, and mixtures thereof.

The detergent bars of the present invention can contain optional surfactants in addition to the anionic synthetic detergent surfactants described above. Such optional surfactants, if present, can be included at levels up to a total of about 10%, preferably from about 0.5% to about 3%, by weight of the total bar composition.

A typical listing of the classes and species of optional surfactants, (e.g. nonionic, zwitterionic and amphoteric surfactants) optional alkaline builders such as sodium carbonate trisodium phosphate, etc. and other ingredients useful herein appears in U.S. Pat. No. 3,664,961, issued to Norris on May 23, 1972, and EP 550,652, published on April 16, 1992.

Amine Oxides are excellent cosurfactants that may be used in conjunction with the present invention. Preferred types are C_{12}-C_{18} amine oxides, preferably C_{14}. If included, the level of amine oxide in the final bar composition is from about 1% to about 10%, preferably, from about 2% to about 5%.

Other synthetic anionic surfactants suitable for use herein as additional optional surfactants are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates. Preparation of alkyl glyceryl ether sulfonates are described in detail in U.S. Pat. 3,024,273, Whyte et al., issued March 6, 1962.

In addition, optional synthetic anionic surfactants include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and paraffin sulfonates containing from about 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl

group and from about 8 to 20 carbon atoms in the alkane moiety.

In addition, a hydrotrope, or mixture of hydrotropes, may be present in the laundry detergent bar. Preferred hydrotropes include the alkali metal, preferably sodium, salts of toluene sulfonate, xylene sulfonate, cumene sulfonate, sulfosuccinate, and mixtures thereof. Preferably, the hydrotrope is added to the linear alkyl benzene sulfonic acid prior to its neutralization. The hydrotrope, if present, will preferably be present at from about 0.5% to about 5% of the laundry detergent bar.

The builder can optionally contain in addition to the phosphate builder, a non-phosphate detergent builder. Specific examples of non-phosphate, inorganic detergency builders include water-soluble inorganic carbonate and bicarbonate salts. The alkali metal (e.g., sodium and potassium) carbonates and bicarbonates are particularly useful herein. Other specifically preferred examples of builders include polycarboxylates.

Sodium carbonate, another optional ingredient, is particularly preferred as a neutralizing inorganic salt for an acid precursor of an anionic surfactant used in such compositions, such as the alkyl ether sulfuric acid and alkylbenzene sulfonic acid. Co-polymers of acrylic acid and maleic acid are preferred in the subject compositions as auxiliary builders.

Binding agents is particularly preferred to give the bar composition good binding and a good rate of hardening during the manufacture of the bar compositions. Preferably the addition of magnesium sulfate to the bar composition gives such benefits. When used, the bar composition comprises from about 1.5% to about 10%, more preferably, from about 2% to about 5% magnesium sulfate, by weight of the final bar composition. When magnesium sulfate is used, it must be added in the manufacturing process after the addition of both the calcium salt, siliceous material, and phosphate detergency builder.

Soil suspending agents can be used. Soil suspending agents can also include water-soluble salts of carboxymethylcellulose and carboxyhydroxymethylcellulose. A preferred soil suspending agent is an acrylic/maleic copolymer, commercially available as Sokolan®, from BASF Corp. Other soil suspending agents include polyethylene glycols having a molecular weight of about 400 to 10,000, and ethoxylated mono- and polyamines, and quaternary salts thereof. If included, it can be at levels up to about 5%, preferably about 0.1-1%.

The bleach agent in the detergent composition, when included, is preferably at a level from about 0.10% to about 60% by weight; more preferably, from about 1% to about 50%; most preferably, from about 1% to about 20%. The bleach agents used herein can be any of the bleach agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. Mixtures of bleach agents can also be used.

A useful bleach agent that can be used encompasses percarboxylic acid bleach agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleach agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleach agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Other peroxygen bleach agents can also be used. Suitable peroxygen bleach compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

Bleach agents other than oxygen bleach agents are also known in the art and can be utilized herein. One type of non-oxygen bleach agent of particular interest includes photoactivated bleach agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

An optional useful percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate,

borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

When included, the preferred bleach agent for the present invention are those peroxygen bleaching compounds which are capable of yielding hydrogen peroxide in an aqueous solution. These compounds are well known in the art and include organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaching compounds, such as the alkali metal perborates, percarbonates, perphosphates, and the like. Mixtures of two or more such bleaching compounds can also be used, if desired.

Preferred peroxygen bleaching compounds to be used in the present invention include sodium perborate, commercially available in the form of mono- and tetra-hydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, and urea peroxyhydrate. Particular preferred are sodium perborate tetrahydrate, and especially, sodium perborate monohydrate. Sodium perborate monohydrate is especially preferred because it is very stable during storage and yet still dissolves very quickly in the bleaching solution.

Another optional component of the present invention is a detergent chelant. Such chelants are able to sequester and chelate alkali cations (such as sodium, lithium and potassium), alkali metal earth cations (such as magnesium and calcium), and most importantly, heavy metal cations such as iron, manganese, zinc and aluminum. Preferred cations include sodium, magnesium, zinc, and mixtures thereof.

The detergent chelant is preferably a phosphonate chelant, particularly one selected from the group consisting of diethylenetriamine penta(methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid), and mixtures and salts and complexes thereof, and an acetate chelant, particularly one selected from the group consisting of diethylenetriamine penta(acetic acid), ethylene diamine tetra(acetic acid), and mixtures and salts and complexes thereof. Particularly preferred are sodium, zinc, magnesium, and aluminum salts and complexes of diethylenetriamine penta(methylene phosphonate) diethylenetriamine penta (acetate), and mixtures thereof.

Preferably such salts or complexes have a molar ratio of metal ion to chelant molecule of at least 1:1, preferably at least 2:1. The detergent chelant can be included in the laundry bar at a level up to about 5%,

preferably from about 0.1% to about 3%, more preferably from about 0.2% to about 2%, most preferably from about 0.5% to about 1.0%.

Another optional component of the laundry bar is fatty alcohol having an alkyl chain of 8 to 22 carbon atoms, more preferably from 12 to 18 carbon atoms. A preferred fatty alcohol has an alkyl chain predominantly containing from 16 to 18 carbon atoms, so-called "high-cut fatty alcohol," which can exhibit less base odor of fatty alcohol relative to broad cut fatty alcohols. Typically fatty alcohol, if any, is present in the laundry bar at up to a level of 10%, more preferably from about 0.75% to about 6%, most preferably from about 2% to about 5%. The fatty alcohol is generally added to a laundry bar as free fatty alcohol. However, low levels of fatty alcohol can be introduced into the bars as impurities or as unreacted starting material. For example, laundry bars based on coconut fatty alkyl sulfate can contain, as unreacted starting material, from 0.1% to 3.5%, more typically from 2% to 3%, by weight of free coconut fatty alcohol on a coconut fatty alkyl sulfate basis.

Another optional component in the laundry bar is a dye transfer inhibiting (DTI) ingredient to prevent diminishing of color fidelity and intensity in fabrics. A preferred DTI ingredient can include polymeric DTI materials capable of binding fugitive dyes to prevent them from depositing on the fabrics, and decolorization DTI materials capable of decolorizing the fugitive dye by oxidation. An example of a decolorization DTI is hydrogen peroxide or a source of hydrogen peroxide, such as percarbonate or perborate. Non-limiting examples of polymeric DTI materials include polyvinylpyrridine N-oxide, polyvinylpyrrolidone (PVP), PVP-polyvinylimidazole copolymer, and mixtures thereof. Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as "PVPI") are also preferred for use herein. The amount of DTI included in the subject compositions, if any, is about 0.05-5%, preferably about 0.2-2%.

Another optional component in the laundry bar is a fabric softener component. Such materials can be used, if any, at levels of about 0.1% to 5%, more preferably from 0.3% to 3%, and can include: amines of the formula $R_4R_5R_6N$, wherein R_4 is C_5 to C_{22} hydrocarbyl, R_5 and R_6 are independently C_1 to C_{10} hydrocarbyl. One preferred amine is ditallowmethyl amine; complexes of such amines with fatty acid of the formula R_7C00H, wherein R_7 is C_9 to C_{22} hydrocarbyl, as disclosed in EP No. 0,133,804; complexes of such amines with phosphate esters of the

formula R_8O-P(O)(OH)-OR_9 and HO-P(O)(OH)-OR_9, wherein R_8 and R_9 are independently C_1 to C_{20} alkyl of alkyl ethoxylate of the formula -alkyl-(OCH_2CH_2); cyclic amines such as imidazolines of the general formula 1-(higher alkyl) amido (lower alkyl)-2-(higher alkyl)imidazoline, where higher alkyl is from 12 to 22 carbons and lower alkyl is from 1 to 4 carbons, such as described in UK Patent Application GB 2,173,827; and quaternary ammonium compounds of the formula $R_{10}R_{11}R_{12}R_{13}N^+X^-$, wherein R_{10} is alkyl having 8 to 20 carbons, R_{11} is alkyl having 1 to 10 carbons, R_{12} and R_{13} are alkyl having 1 to 4 carbons, preferably methyl, and X is an anion, preferably Cl^- or Br^-, such as C_{12-13} alkyl trimethyl ammonium chloride.

Sodium sulfate is a well-known filler that is compatible with the compositions of this invention. It can be a by-product of the surfactant sulfation and sulfonation processes, or it can be added separately. Calcium carbonate (also known as Calcarb) is also a well known and often used filler component of laundry bars. Filler materials are typically used, if included, at levels up to 40%, preferably from about 5% to about 25%.

Optical brighteners are also optional ingredients in laundry bars of the present invention. Preferred optical brighteners are diamino stilbene, distyrilbiphenyl-type optical brighteners. Preferred as examples of such brighteners are 4,4'-bis{[4-anilino-6-bis(2-hydoxyethyl) amino-1,3,5-trizin-2-yl]amino}stilbene-2,2'-disulfonic acid disodium salt, 4-4'-bis(2-sulfostyryl) biphenyl and 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl) amino]stilbene-2,2'-disulfonic acid disodium salt. Such optical brighteners, or mixtures thereof, can be used at levels in the bar of from about 0.05% - 1.0%.

Dyes, pigments, germicides, and perfumes can also be added to the bar composition. If included, they are typically at levels up to about 0.5%.

Another useful optional component of the subject compositions are detergent enzymes. Particularly preferred are lipase, protease, amylase, and mixtures thereof. Enzymes, if included, are typically at levels up to about 5%, preferably about 0.5-3%.

Moisture

The final bar composition should have no more than about 15% moisture. The moisture level of the total bar composition can be determined by any methods known in the art by one skilled in the area of laundry bar compositions. One common method is the Bidwell Sterling Distillation method. Another known method is the Karl Fischer Moisture Titration

Method. See AOCS official method Dd2a-59 issue 93 and AOCS official method Dd2b-59 issue 89.

Bar Physical Properties

The bars of the present invention are sufficiently hard. A preferred method to measure bar hardness is to measure the penetration of a needle through the bar surface under a standard weight for 5 seconds using a cone penetrometer. One such penetrometer is made by Associated Instrument Manufacturers India Pvt. Ltd. (Model number AIM 512). The weight of the rod and the cone is 149 grams and an additional 50 gram weight is placed on the cone. The penetration reading of a fresh bar made as per the present invention will typically be about 20-30 (1/10 mm) and after 40 minutes it would be around 15-20 (1/10 mm) . Bars aged about 3 days at ambient conditions will typically have a bar penetration reading of about 5-12 (1/10 mm).

Another physical property of interest is the bar solubility in water. One method of determining the bar solubility is to submerge a bar having the following dimensions: 75mm x 55mm, in 250 ml of water in a beaker for 2 hours, drying the bar at 60 degrees C for 2 hours and then weighing the bar. To have acceptable bar solubility, the difference in weight should be about 15-20 grams for a 125 gram bar (12-16% of the original weight of the bar), more preferably 5-15 grams (4-12% of the original weight of the bar).

Yet another physical property of consumer relevance is the rate of drying of the bar after usage and storage under high humidity conditions. A preferred method to measure this property is to place a bar with dimensions of 75mm x 55mm with one of its large flat surface in contact with about 20 ml of water in a petri dish for 2 hours and then scraping the gel formed. This procedure is repeated for a second cycle except that the gel is not scraped off from the bar surface after the second contact with water. The bar is then stored under 30 degrees C and 88% Relative Humidity for 24 hours and then the bar surface which was exposed to the water is graded for dryness on a 1-5 grading scale by experienced operators as illustrated below:

Dryness Grade	Physical state of the bar surface
1	very wet, very soft, melting, soft core
2	wet, soft gel, hard core
3	somewhat dry (moist), feels soft
4	somewhat dry (moist), feels hard

5 completely dry, hard

For good consumer acceptance, the dryness grade is typically between 3.5-5.0. Preferred bars of the present invention have a dryness grade within this range.

Processing

The detergent laundry bars of the present invention can be processed in conventional soap or detergent bar making equipment with some or all of the following key equipment: blender/mixer, mill or refining plodder, two-stage vacuum plodder, logo printer/cutter, cooling tunnel and wrapper.

In a typical process the raw materials are mixed in the blender. Alkyl benzene sulfonic acid is reacted with alkaline inorganic salts to complete neutralization, the amount of alkaline inorganic salt being at least sufficient to completely neutralize the acid. Once the neutralization reaction is completed, a polyol and a cross-linking agent can optionally be added. For example, by adding a polyol and a cross-linking agent to the mixture prior to the addition of the calcium salt and silaceous material. The calcium salt and siliceous material are then added to form a complex in-situ. To control the grit formation during this reaction, it is preferable to add some inert powdered materials like talc and/or zeolite after the addition of silicate, but before the addition of the calcium salt. Preferably the level of these inert materials should be from about 1% to about 20%, by weight of the composition. The calcium salt and siliceous material must be added to a completely neutralized anionic active. Therefore, they should only be added after the neutralization of the acid form of anionic synthetic detergent surfactant. Where pre-neutralized anionic surfactant is used exclusively, the calcium salt and siliceous material can be added either before or after the surfactant is added to the mixer. Phosphate detergency builder is added after the addition of calcium salt and siliceous material. Then other optional surfactants followed by any additional optional components such as chelants are added. The mixing can take from one minute to one hour, with the usual mixing time being from about two to twenty minutes. The blender mix is charged to a surge tank. The product is conveyed from the surge tank to the mill or refining plodder via a multi-worm conveyor.

After milling or preliminary plodding, the product is then conveyed to a two-stage vacuum plodder, operating at high vacuum, e.g. 600 to 740 mm of mercury vacuum, so that entrapped air/gas is removed. The product is

extruded and cut to the desired bar length, and printed with the product brand name. The printed bar can be cooled, for example in a cooling tunnel, before it is wrapped, cased, and sent to storage.

A preferred laundry bar composition is made by the following method: The raw materials are first mixed in a blender. Sodium carbonate and pre-neutralized coco fatty alkyl sulfate (CFAS) (if a mixture of CFAS/LAS is used as a surfactant system) are mixed for about 1-2 minutes. This is followed by the addition of linear alkyl benzene sulfonic acid and sulfuric acid (if present in the formulation). The acids are then completely neutralized by the sodium carbonate in the seat of the blender. (The amount of sodium carbonate should be at least an amount sufficient to neutralize the acids.) Once the neutralization reaction is completed, sodium silicate is added, followed by the addition of talc and zeolite, and the mixture is mixed for about 2 minutes. $Ca(OH)_2$ is then added and mixed for an additional 2 minutes. Then, a chelant, if present is added, followed by other optional surfactants, STPP, magnesium sulfate, and any other additional optional components. The STPP and magnesium sulfate (when used) must be added after the addition of $Ca(OH)_2$ and siliceous material is mixed to form a complex in situ. Magnesium sulfate, when used is also added after the STPP. The total mixing time can take up to about one hour, with the usual mixing time being from about five to twenty minutes. As one of the last optional ingredients, bleach and enzymes can be added to the mixture and then mixed for an additional one to five minutes. The blender mix is charged to a surge tank. The product is conveyed from the surge tank to the mill or refining plodder via a multi-worm conveyor.

After milling or preliminary plodding, the product is then conveyed to a two-stage vacuum plodder, operating at high vacuum, e.g. 600 to 740 mm of mercury vacuum, so that entrapped air is removed. The product is extruded and cut to the desired bar length, and printed with the product brand name. The printed bar can be cooled, for example in a cooling tunnel, before it is wrapped, cased, and sent to storage.

Examples of the invention are set forth hereinafter by way of illustration and are not intended to be in any way limiting of the invention.

EXAMPLE I

The invention is illustrated by the following non-limiting examples. All parts and percentages herein are by weight unless otherwise stated.

The following compositions are prepared by the process of the invention.

	A	B	C
	(weight percent)		
Linear alkyl benzene sulfonate	12.5	0	8.5
Coco fatty alkyl sulfate	12.5	18	16.0
C14 amine oxide	0	5	0
Soda Ash	14	14	15
Sulfuric acid	2.5	2.5	2.5
Sodium Tripolyphosphate	11.6	11.6	11.6
Calcium carbonate	31	27	14
Coco fatty alcohol	1	1	1
Zeolite	2	2	2
Alkaline sodium silicate (48% solids)*	3	6	10
Calcium hydroxide	1.5	3	5
TiO_2	1	1	1
Perborate Monohydrate	2.25	4.5	10
Fluorescent agents	0.2	0.2	0.2
Perfume	0.35	0.35	0.35
Moisture (final comp.)	3.5	4.5	6.0
Diethylenetriamine pentaacetate	0.9	0.9	0.9
Other conventional ingredients	Balance	Balance	Balance
	100	100	100

*amount of silicate solids

EXAMPLE II

The following compositions are prepared by the process of the invention.

	D	E
	(weight percent)	
Linear alkyl benzene sulfonate	19	19
Soda Ash	13.7	12
Sodium Tripolyphosphate	14	14
Calcium carbonate	32	28
Sodium Sulfate	3	3
Zeolite	2	2
Alkaline Sodium Silicate(48% solids)*	3	7
Calcium Hydroxide	1.5	3
Talc	10	10
Anhydrous Magnesium sulfate	2	3
Fluorescent agents	0.2	0.2
Perfume	0.35	0.35
Moisture (final comp.)	3	5
Other conventional ingredients	balance	balance
	100	100

*amount of silicate solids

EXAMPLE III

The following compositions are prepared by the process of the invention.

	F	G
	(weight percent)	
Linear alkyl benzene sulfonate	21	21
Soda Ash	12	12
Sodium Tripolyphosphate	20	20
Calcium Carbonate	3.7	-
Sodium Sulfate	3	3
Calcium Sulfate	5	10
Powdered Sodium Silicate (78% solids)*	3.46	3.46
Calcium Hydroxide	3.45	3.45
Talc	10	1.6
Anhydrous Magnesium Sulfate	3	3
Fluorescent agents	0.225	0.225
Perfume	0.35	0.35
Moisture (final comp.)	4.75	4.75
Poly Ethylene Glycol	-	1.0
Polyvinyl Alcohol	0.6	-
Sodium Borate	1.5	-
Boric Acid	-	1.5
Other conventional ingredients	balance	balance
	100	100

*amount of silicate solids

WHAT IS CLAIMED IS:

1. A process for making a synthetic laundry detergent bar composition comprising the steps of:

a. forming a mixture comprising a neutralized anionic synthetic detergent surfactant selected from the group consisting of alkyl sulfate, linear alkyl benzene sulfonate, and mixtures thereof, a phosphate detergency builder, calcium salt, siliceous material, and optionally other ingredients;

wherein the calcium salt and siliceous material form a complex in-situ; and

wherein the phosphate detergency builder is added after the addition of calcium salt and siliceous material; and

b. forming into bars;

wherein the bar comprises at least 6% of the anionic synthetic detergent surfactant in the final bar composition.

2. A process according to Claim 1, wherein the anionic synthetic detergent surfactant is selected from the group consisting of C_{10-18} alkyl sulfate, C_{10-18} linear alkyl benzene sulfonate, and mixtures thereof.

3. A process according to Claim 1, wherein the calcium salt is selected from the group consisting of CaO, Ca(OH)2, $CaCl_2$ and $CaSO_4$, and mixtures thereof.

4. A process according to Claim 1, further comprising the step of adding a polyol and a cross-linking agent to the mixture.

5. A process according to Claim 4, wherein the polyol and the cross-linking agent are added to the mixture prior to the addition of the calcium salt and silaceous material, wherein the polyol is selected from the group consisting of sorbitols, polymers with free hydroxyl groups, substituted polyols, and mixtures thereof, and wherein the cross-linking agent is selected from the group consisting of oxophiles, acids, and mixtures thereof.

6. A synthetic laundry bar composition as claimed in Claim 1.

7. A synthetic laundry bar composition as claimed in Claim 4, further comprising from about 0.10% to about 60% bleach agent.

8. A process for making a synthetic laundry detergent bar composition comprising the steps of:

a. forming a mixture comprising a neutralized anionic synthetic detergent surfactant selected from the group consisting of alkyl sulfate, linear alkyl benzene sulfonate, and mixtures thereof, a phosphate detergency builder, calcium salt, siliceous material, magnesium sulfate, and optionally other ingredients;

wherein the calcium salt and siliceous material form a complex in-situ; and

wherein the phosphate detergency builder is added after the addition of calcium salt and siliceous material;

wherein the magnesium sulfate is added after the addition of the phosphate detergency builder;

wherein a powdered inert material is added after the siliceous material but before the addition of the calcium salt; and

b. forming into bars;

wherein the bar comprises at least 6% of the anionic synthetic detergent surfactant in the final bar composition.

9. A process for making a synthetic laundry detergent bar composition comprising the steps of:

a. forming a mixture comprising an acid form of an anionic synthetic detergent surfactant selected from the group consisting of alkyl sulfate, linear alkyl benzene sulfonate, and mixtures thereof; a non-phosphate alkaline salt for neutralizing the acid form of the anionic synthetic detergent surfactant; from about 5% to about 50% phosphate detergency builder selected from the group consisting of water-soluble alkali-metal salts of phosphate, pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof; calcium salt; siliceous material; and optionally other ingredients;

wherein the calcium salt and siliceous material form a complex in-situ after neutralization of the anionic synthetic detergent surfactant; and wherein the phosphate detergency builder is added after the addition of calcium salt and siliceous material; and

b. forming into bars;

wherein the bar comprises from about 15% to about 30% of anionic synthetic detergent surfactant in the final bar composition.

10. A synthetic laundry detergent bar composition made by the process as claimed in Claim 8, further comprising from about 1% to about 10% amine oxide.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03100

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C11D/12
US CL :510/141, 155, 156, 447, 440

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/141, 155, 156, 447, 440

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: polyvalent, calcium, mangesium, amine oxide#, polyol#

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,721,202 A (WAITE ET AL) 24 February 1988, abstract, col. 2-col. 4, example 3.	1-10
Y,P	US 5,670,466 A (SIVIK ET AL) 23 September 1997, columns 2-5, examples and claims.	1-10
Y	US 3,926, 861 A (GERECHT) 16 December 1975, columns 2-4, example and claims.	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"B"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

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27 APRIL 1998

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Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
NECHOLUS OGDEN
Telephone No. (703) 308-0661

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